

CONCENTRATION OF BIOPETROL SYNTHESIZED FROM PALMITIC ACID
THROUGH CATALYTIC CRACKING USING ZEOLITE AS CATALYST

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A thesis submitted in fulfillment of the
requirements for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
Universiti Malaysia Pahang

APRIL 2009

DECLARATION

I declare that this thesis entitled “*Concentration Of Biopetrol Synthesized From Palmitic Acid Through Catalytic Cracking Using Zeolite As Catalyst*” is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature :

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Date : 28 APRIL 2009

DEDICATION

To my beloved father and mother

ACKNOWLEDGEMENT

Bismillahirrahmanirrahim and Alhamdulillah. Praise be to God for His help and guidance that I finally able to complete this Undergraduate Research Project.

First and foremost I would like to extend our sincerest gratitude to Mr. Syaiful Nizam Hassan, my supervisor for his willingness in overseeing the progress of my works from its initial phases till the completion of it. I do believe that all his advice and comments are for the benefit of producing the best thesis quality.

I want to express gratitude to my mother, Madam Kalthum binti Aluan, and the rest of my family for their unconditional support and encouragement in whatever I do. For my late father, Suhaimi bin Pardi, I pray to God so that this work will send to you for your good reward, ameen.

I would like to also take this opportunity to thank all lecturers who involved directly and indirectly in helping me to complete this research. For fersonnel at FKKSA technical staff especially Miss Hafizah binti Ramli, Mr. Abd Razak bin Abd Hamid, and Mohd Anuar bin Hj. Ramli. Thank you very much for your guidance, trust, and assistance.

To my friends and course mates, that giving endless helps and support, thank you very much, especially under same supervisor, Nur Aini Liyana binti Zakaria, Redza Shah Azmeer bin Hasanudin, Normalina binti Norzal, and Nurul Liana Abd Rahman.

Thanks to former and present colleagues at Universiti Malaysia Pahang for making an enjoyable working environment and giving me ideas opinions, and advices. Thank you again.

ABSTRACT

Biofuel is defined as fuel produced from derivation of vegetable oils and specifically, biopetrol is defined as fuel which has the same characteristic with the petrol, but is produced from palmitic acid that is dominated in palm oil where the conversion of palmitic acid is done to get the molecular formula and structure of isooctane. Due to depletion of fossil fuel, environmental issues, and rising of petrol price, biopetrol can be the alternative fuel to the fossil fuel. Catalytic cracking method is conducted in this research due to the low yields from thermal cracking method. Furthermore, Malaysia is plenty with palm oil which palmitic acid is dominated in palm oil composition. In recent years, there have been several other studies on the production of hydrocarbons from palm oil mainly bio-gasoline (biopetrol) which have been carried out using cracking catalysts. Zeolites have shown excellent performance as solid acid cracking catalysts due to their higher selectivity. Many researcher have studied that catalytic cracking method will produce much higher yields than thermal cracking method. Through catalytic cracking process, palmitic acid is catalytic cracked with 4 different amount of catalyst – 1g, 5g, 10g, and 20g. The distilled product is diluted with 4 different dilution mixture solution – 1%, 5%, 10%, and 20%. All the product samples are analyzed with Gas Chromatographer (GC). The isooctane concentrations are increased when the amount of catalysts are increased, but not obviously. The lowest percentage concentration of isooctane obtained is 9.1822 % and the highest percentage concentration of isooctane obtained is 20.7210 %. These yields are much higher than the yields produced from thermal cracking method which is 3% to 5 %. It showed that the catalytic cracking method will produce much higher yields for biopetrol synthesized compared to thermal cracking method. This experiment should be conducted in dynamic state to optimize the yields.

ABSTRAK

Biofuel didefinisikan sebagai bahan api yang dihasilkan daripada terbitan oleh minyak sayuran. Secara spesifiknya biopetrol didefinisikan sebagai bahan api yang mempunyai sifat yang sama dengan petrol tetapi ia dihasilkan daripada asid palmitik di mana komposisinya banyak terdapat pada minyak sawit. Pertukaran asid palmitik dilakukan dengan mendapat formula molekul dan struktur isooktana. Oleh kerana sumber bahan api fosil yang semakin kurang, isu alam sekitar, kenaikan harga petrol, biopetrol boleh menjadi bahan api alternatif kepada bahan api fosil. Kaedah penghuraian berkatalis digunakan dalam kajian ini disebabkan hasil yang dijana daripada kaedah penghuraian haba adalah rendah. Tambahan pula Malaysia kaya dengan sumber minyak sawit di mana asid palmitik mendominasi komposisi di dalamnya. Dewasa ini, terdapat kajian berkenaan penghasilan biopetrol daripada hidrokarbon minyak sawit. Kajian dijalankan menggunakan penghuraian berkatalis. Katalis zeolite telah menunjukkan hasil yang cemerlang sebagai katalis penghuraian asid pepejal kerana kadar selektif/pemilihannya yang tinggi. Banyak penyelidik telah menemui bahawa kaedah penghuraian berkatalis dapat menghasilkan produk yang lebih tinggi daripada kaedah penghuraian haba. Semasa penghuraian berkatalis, asid palmitik dihuraikan secara berkatalis dengan menggunakan 4 kandungan katalis yang berbeza – 1g, 5g, 10g, dan 20 g. Hasil yang disulingkan dicairkan dengan menggunakan kepekatan yang berbeza – 1%, 5%, 10%, dan 20%. Semua sampel produk dianalisis dengan menggunakan *Gas Chromatographer*. Kepekatan isooktana yang dikehendaki akan bertambah apabila kandungan katalis yang digunakan bertambah, tetapi tidak terlalu jelas. Peratus kepekatan isooktana yang terendah didapati adalah 9.1822% manakala yang tertinggi adalah 20.7210%. Penghasilan ini adalah lebih tinggi daripada hasil yang diperolehi daripada penghuraian haba iaitu 3% - 5%. Ini menunjukkan kaedah

penghuraian berkatalis adalah lebih baik. Eksperimen ini patut dijalankan dalam keadaan dinamik untuk mendapatkan hasil yang optimum.

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LIST OF ABBREVIATIONS

Al ₂ O ₃	-	Alumina
CEC	-	Cation Exchange Capacity
CO ₂	-	Carbon dioxide
FID	-	Flame Ionization Detector
GC	-	Gas Chromatographer
H ₂	-	Hydrogen
H ₂ SO ₄	-	Sulfuric acid
HF	-	Hydrofluoric acid
LPG	-	Liquid Petroleum Gas
N ₂	-	Nitrogen
PETRONAS	-	Petroliaam Nasional Malaysia Berhad
PORIM	-	Palm Oil Research Institute
Pt	-	Platinum
RPM	-	Revolution per minute
SiC	-	Silicon Carbide
SiO ₂	-	Silica

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CHAPTER I

INTRODUCTION

1.1 Introduction

Generally, biofuel is defined as fuel produced from derivation of vegetable oils and specifically, biopetrol is defined as fuel which has the same characteristic with the petrol, but is produced from palmitic acid that is dominated in palm oil where the conversion of palmitic acid is done to get the molecular formula and structure of isooctane.

Biopetrol is produced to be the alternative fuel to the fossil fuel for vehicle-engine purposes whether it is produce with the same performance to fossil fuel or with unrivalled performances.

Due to its environmental merits, the share of biofuel in the automotive fuel market will grow fast in the next decade. There are several reasons for biofuels to be considered as relevant technologies by both developing and industrialized countries. Biofuels include energy security reasons, environmental concerns, foreign exchange savings, and socioeconomic issues related to the rural sector. The biofuel economy will grow rapidly during the 21st century. Its economy development is based on agricultural production and most people live in the rural areas.

Biodiesel is one of the biofuel. The application of existing biodiesel from palm oil in motor vehicle has been proven to be successful. However, the biodiesel used is

limited for diesel-used vehicles only, so the same approach must be done for petrol-used vehicles.

Biofuel produced from natural vegetable oil or fats can be used as transportation fuel or fuel additive in the vehicles to reduce their emissions. Plant oils are attracting increased attention in this respect (Bhatia *et al.*, 2003). Plant oils are those oils that are derived from plant resources such as palm oil. Realizing that palm oil is one of the nation's economic pillars and catalyst of rural development, Palm Oil Research Institute of Malaysia (PORIM) has developed a process based on palm oil, as a substitute diesel by converting it into methyl esters (biodiesel) by reaction with methanol and have extensively tested as a substitute for diesel (Choo and Ma, 1996). Biodiesel is suitable for diesel engines. The gasoline engines need bio-gasoline (biopetrol) to be produced from palm oil. In recent years, there have been several other studies on the production of hydrocarbons from palm oil mainly bio-gasoline (Twaiq *et al.*, 1999; Yean-Sang, 2004) which have been carried out using cracking catalysts in a micro-reactor. Zeolites have shown excellent performance as solid acid cracking catalysts due to their higher selectivity (Leng *et al.*, 1999).

Various catalysts are reported for cracking of triglycerides. The choice of the catalyst plays an important role in the cracking of triglyceride. Since zeolites are extremely active, therefore it has been tested extensively for catalytic cracking, especially of vegetable oil by several researchers (Twaiq *et al.*, 1999; Yean-Sang *et al.*, 2004).

1.2 Identification of Problem

1.2.1 Rising of Petrol Oil Prices

Years by years until now, the petrol oil have been spiralled in prices. It will cause many domino effect in terms of goods and services cost and will interrupt the global economic growth and stability. The highest crude oil price in ever history until now that has been written on Jun 30, 2008 that is 143 US Dollar per barrel. This will also increase all the petroleum-based product prices. Mostly affected are diesel and petrol. Figure 1.1 shown the price of world crude oil from 1994 to March 2008 and Figure 1.2 shown the petrol price in Malaysia from May 2004 to Jun 2008.



Figure 1.1: Price of World Crude Oil from 1994 to March 2008



Figure 1.2: Petrol Price in Malaysia from May 2004 to Jun 2008

One of the major factors that caused this rising is the limitation of the fossil fuel reserves and high demand for the petroleum-based product. Fossil fuel are non-renewable energy resources because the formation fossil fuels will take millions of years, and the fossil fuel reserves are being depleted much faster than new one being formed. According to Malaysia's situation, if Petroliaam Nasional Malaysia Berhad (PETRONAS) does not discover new fuel oil reserve, the Malaysia oil reserve will end around 20 until 22 years later and fully become net importer petroleum country.

Due to the rising of the development growth around the world, the demand of petroleum-based product was increased especially gasoline (greatest demand of gasoline caused over 50% of the crude oil be converted into it). The drastic economic growth from the India and China will effect one of the major petroleum limited supply according to the recent global situation. Worldwide energy demand, driven by the population growth and industrialization of the developing world, will expand by 40% in

the next 20 years. This will occur the unbalance of demand and supply. The helps to monitor increasing fuels' prices were reports that petroleum production is at (Deffeyes Kenneth S, 2007) or near full capacity (Gold Russell and Davis Ann, 2007). Global consumption of oil rose from 30 billion barrels ($4.8 \times 10^9 \text{ m}^3$) in 2004 to 31 billion in 2005 (Wikipedia, 2008).

Many series of unstable geopolitical issues and war around the world. These including, the collapsing of World Trade Centre (WTC) on US on September 11, 2001; the war in Iraq; the crisis between Israel and Lebanon; the nuclear brinkmanship between US and Iran and other unstable geopolitical issues. It is not refused also that the rising of oil prices is due to the speculative activities from someone party(s) (Hassan Marican, 2008).

1.2.2 Environmental Issue

Gasoline is one of the sources of pollutant gases. Gasoline produces carbon dioxide, nitrogen oxides, and carbon monoxide in the exhaust of the engine which is running on it. Carbon emissions have been increasing ever since the industrial revolution. Today, the atmosphere contains about 380 parts per million of carbon dioxide and still increases by approximately two parts per million annually. During this time frame, the global average temperature has risen by more than 1°F since carbon dioxide traps heat near the Earth's surface (Wikipedia, 2008). Our Earth will be faced with an enormous rise in sea level due to the melting of Greenland and West Antarctic ice sheets and icebergs. Furthermore, unburnt gasoline and evaporation from the tank, when in the atmosphere, react in sunlight to produce photochemical smog.

1.2.3 Low Yields from Thermal Cracking Method

The related previous research has been done to produce biopetrol from palmitic acid using thermal cracking method. But they does not produce much of biopetrol quantity which yields just around 3 to 5 percents (Zariyati, 2008).

1.3 Objectives

- i) To improve the concentration of isooctane produced from palmitic acid by using catalytic cracking method.
- ii) To compare the yields of isooctane produced using catalytic cracking method with the thermal cracking method.

1.4 Scopes of Study

- i) To describe the molecular arrangements of the substances in cracking process.
- ii) To understand the catalytic cracking and distillation process.
- iii) To apply the catalytic cracking process.
- iv) To determine the isooctane composition using Gas Chromatography after palmitic acid is catalytic cracked.

1.5 Rationale and Significance

The problems stated in section 1.1 above have led to an intensified search for viable alternative sources of energy global. This research can be resolved the problem – produce biopetrol from palmitic acid using catalytic cracking method. Biopetrol can be alternative choice to the petrol from the fossil fuel. So, the depending on petroleum uses can be reduced. It might be wise for Malaysia to adopt an implement the use of renewable fuel resources. In this case, Malaysia exploits further utilization of its crude palm oil in automotive sector through research and development by authorities related with palm oil industry. The result is the engine oil and biodiesel. Today, the biodiesel production from palm oil in Malaysia has been established, industrialized in big scale and commercialized to Europe (Yusof B, 2006). However, the biodiesel used is limited for diesel-used vehicles only, so the same approach must be done for petrol-used vehicles by biopetrol.

Malaysia currently accounts for 51 % of world palm oil production and 62% of world exports, and therefore also for 8% and 22% of the world's total production and exports of oils and fats. As the biggest producer and exporter of palm oil and palm oil products, Malaysia has an important role to play in fulfilling the growing global need for oils and fats in general (aseansources.com, 2008). So, Malaysia has big opportunity to produce biopetrol from palmitic acid because it has enough resources to produce in large scale. Palm oil could become the top choice of biofuel producers because world have plenty of palm oil. Below is the oil palm data versus other oilseed crops in the world.

Biopetrol is an environmentally friendly alternative liquid fuel. There has been renewed interest in the use of vegetable oils for making biopetrol due to its less polluting and renewable nature as against the conventional petroleum diesel fuel. The biggest difference between biofuels and petroleum feedstocks is oxygen content. Biofuels have oxygen levels from 10% to 45% while petroleum has essentially none making the chemical properties of biofuels very different from petroleum. All have very low sulfur levels and many have low nitrogen levels (Trabzon, 2007). The CO₂ reduction potential